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FINAL REPORT

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AUTHORS OF REPORT: Dean W. Matson and Richard D. Smith

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FOREWARD:

The development of new methods for producing fine powders and other submicroscale components is essential in a number of advanced technologies. Among these are ceramic and metallurgical applications, where the purities, sizes, and size distribution of particles used for the forming and sintering of compacts can strongly influence the sintering characteristics and physical properties of the resulting product. One novel approach to the production of submicroscale particles and fibers is the rapid expansion of supercritical fluid solutions (RESS) process, which is under development at Battelle-Northwest. This process exploits the abrupt drop in solvent density which occurs when a supercritical fluid (dense gas) is expanded across a nozzle to initiate the nucleation and growth of solute species dissolved in the supercritical fluid solvent prior to expansion.

This report summarizes the results of a three year ARO sponsored study of the RESS process as a method for forming ceramic and preceramic products. Among the goals of the program were the development of an improved understanding of physical processes occurring during the RESS expansion and the utilization of that understanding to allow optimization of RESS product characteristics for specific materials applications. A major emphasis was placed on characterizing the variations in RESS product morphologies which occur with changes in the conditions under which the RESS expansion takes place. This was considered a reasonable approach to establishing the

boundaries of product morphologies which the RESS process is capable of generating, as well as providing empirical evidence into the physical processes occurring during the RESS expansion and at product collection surfaces. Additional emphasis in this project was directed toward investigating the range (and limits) of materials and supercritical solvents suitable for processing by the RESS technique and the development of improved apparatus for specialized applications.

In the course of this program, considerable insight was obtained into the physical aspects of RESS processing, as is reflected in the development of the RESS experimental apparatus over the last three years. The basic components of all RESS apparatus are similar, according to the fundamental requirements of the process. However, considerable flexibility exists with regard to the method for introducing the solute species into the fluid solvent, as well as the design of the nozzle used to produce the expansion. Consequently, considerable experience was obtained in designing RESS apparatus for a range of fluids, and on scales ranging from bench-top to systems capable of liquid throughputs on the order of several liters per minute.

One design development that was found to be particularly useful was a linear autoclave suitable for use with aqueous solvents to pressures of 10,000 psi and temperatures of up to 300°C. These autoclaves, which were constructed from ten foot lengths of 9/16 inch O.D. Hastelloy or 316 stainless steel, could be packed with solids having low fluid solubilities under ambient conditions. Mounted in-line, between the system pump and the expansion region of the apparatus, linear autoclaves were resistively heated by the output from a D.C. power supply and allowed continuous steady state operation of the system for extended periods of time.

Various designs of RESS expansion nozzles were investigated, ranging from capillary-style nozzles having length-to-diameter ratios in excess of 100 to near "pin point" nozzles having comparable lengths and orifice diameters. Laser-drilled sapphire inserts were also investigated for use as RESS nozzles. Nozzle dimensions and design were typically constrained by pumping capacities, flow requirements, material compatibility with the different solvents used, and the ability to seal the nozzle to the end of a heated and pressurized length of metal tubing. Within those limitations, little evidence was found to indicate that nozzle dimensions significantly affected the product characteristics, especially when a particulate or powder product was obtained. Interestingly, the production of high aspect ratio polymer fibers does apparently require the use of capillary-style nozzles on which the nucleated liquid polymer can coat the inner nozzle surface.



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An effort was made during the course of the program to establish the breadth of applicability of this technique to different materials, as well as to determine these limitations. Considerable effort was expended on investigations of supercritical water and carbon dioxide as RESS solvents because these are attractive from economic and environmental perspectives, as well as their having known solubility characteristics toward many solutes of interest, including oxides and polymeric materials. Other solvents, including a number of low molecular weight hydrocarbons, alcohols, and ammonia, were investigated for processing solid materials which were not suitable for use with water or carbon dioxide.

To obtain a powder product during a RESS expansion, it was determined that the solute must be present in the supercritical fluid prior to expansion at some minimum concentration limit in order to nucleate and grow during the expansion. This concentration limit may be as low as a few ppm for some solutes, but is solute dependent (or vapor pressure) and may be much higher for other materials. Many inorganic solutes (most oxides, nitrides, etc.) have solubilities which are too low in pure supercritical solvents having reasonable critical parameters for practical large-scale fine powder production. However, that does not preclude the use of at least some of these essentially insoluble materials for the production of small quantities of ultrafine particles or thin films. In RESS film formation processes in which the solute nucleation occurs heterogeneously at a substrate surface, concentrations of more than a few parts per million in the expanding fluid are neither required nor desirable. The formation of films by RESS expansions of more highly concentrated solutions is promoted by processing conditions favoring the presence of liquid solvent at the substrate surface.

In addition to conventional inorganic ceramic materials (such as oxides), the RESS process was investigated under the ARO program for its potential in polymer processing, with particular emphasis on preceramic polymers. These materials were found to form powders similar to those obtained from inorganic materials by the same nucleation and growth processes. In addition, however, most polymers could also be made to form fine fibers having large aspect ratios. Many polymers were found to be soluble in liquid organic solvents such as pentane and could therefore be prepared in solutions which were pumped directly into the heated region of the RESS apparatus without requiring the use of an autoclave. Other polymers were observed to exhibit sufficient solubility in supercritical carbon dioxide to allow use of this attractive solvent for RESS processing. In general, it was found that polymer fiber formation occurs under RESS expansion temperatures near the polymer melting temperature and that particle formation occurs at expansion temperatures both above and below that

point. Near the polymer melting temperature, where liquid polymer viscosities are high, shear forces produced during the expansion can "draw out" the liquid droplets, which rapidly solidify in the form of short fibers. Alternatively, when capillary-style expansion nozzles are used, liquid polymer precipitation occurs along the length of the capillary. This results in the inner surface of the nozzle becoming coated with the liquid polymer, which is again drawn out by the shear forces of the expanding fluid into essentially continuous fibers.

A particularly interesting development in the RESS project was a demonstration of the ability to produce intimate mixtures of solute materials by co-nucleation during the rapid expansion process. This "compositional quenching" is a solution-based equivalent to rapid quenching techniques used to form thermodynamically unstable glasses or metal alloys from the molten state. Using the RESS technique, mixed oxide, salt-oxide, organometallic complex-oxide, and polymer-polymer molecular composites were prepared. This is a particularly promising area of future application for the RESS process, providing unique opportunities for the production of intimately mixed materials. It was also found that the addition of small quantities of a second solute may, under some conditions, alter the morphologies of RESS products. Descriptions of these and other developments have been detailed in papers prepared for publication during the course of this program.

Publications prepared under contract No. DAAL03-86-K-0033:

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